ADHERENCE AND PROPERTIES OF SILICON CARBIDE BASED FILMS ON STEEL

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Abstract - Coatings of silicon carbide with various compositions have been obtained in a r.f plasma assisted process using tetramethylsilane and argon as input gases. Some properties against mechanical applications of such deposits on steel have been investigated. Residual stresses and hardness are reported and discussed in relation with plasma parameters and deposit composition. By scratch testing, it was shown that the silicon carbide films on steel denote a good adherence when compared with previous data encountered in the literature for titanium carbide or nitride deposits though low critical load values. Adherence is discussed in relation to the nature of the interfacial zone examined by Auger depth profiling. It is concluded that the films have promising variable properties which can be optimized by acting on plasma parameters.

1.- Introduction.

The plasma assisted CVD technique presents wide interest in order to obtain hard thin layers on steel for mechanical applications.

Silicon carbide coatings have been produced on construction steel substrates in a cold wall reactor through a r.f glow discharge of TMS [$\text{Si}(\text{CH}_3)_4$] and Ar.

In a previous study ¹ the main factors influencing the process were determined and their effects on deposition rates (R) and coating compositions (c) were established. Furthermore (R) can be described as a function of the plasma parameters by a "global" kinetic approach in a perfect plug flow reactor based on typical reaction schemes (this proceedings). At first, it is worthwhile to recall some experimental features of the device used. The r.f discharge is generated by induction in a gaseous flow ($F_T = 1.4 \text{ cm}^3 \cdot \text{s}^{-1}$) under medium pressure ($P > 100 \text{ Pa}$). The substrate is set backward in the coil, so the temperature is related with its position and the input power.

In the applied conditions the radical concentration is higher than the ion concentration. The growth process will occur through radical reaction paths activated by ion bombardment.

2.- Composition of coatings.

Temperature increases the carbon content while decreasing the silicon content ($600 < T < 1100 \text{ K}$, $1.35 < \text{Si/C} < 0.9$). As position and temperature are connected, the Si/C variation may be attributed to successive dissociations along the plasma leading thus to the adsorption-reaction of different fragments on the substrate ¹.

As temperature is high enough no hydrogen is trapped. IR spectra of coatings obtained on monocrystalline silicon substrates do not reveal hydrogen bonds for the films produced at temperature above 673 K. Though large enough the peak centered at 770 cm^{-1} (Si-C bonds) is nevertheless narrow in regards to those encountered for " $\alpha\text{-Si}_x\text{C}_{1-x}\text{H}$ "^{2,3}. X-ray diffraction patterns (Co K α) of the samples are constituted by a broad peak ($2\theta \approx 41.5^\circ$, $\Delta(2\theta) \approx 4^\circ$) which increases with deposition temperature. Auger and ESCA spectroscopies suggest respectively that the $\text{Si/C} > 1$ samples contain free silicon (on the basis of carbon and silicon intensities) and the $\text{Si/C} < 1$ free carbon (on the basis of the position and peak shape).

The deposition pressure ($100 < P < 1300\text{ Pa}$) weakly affects the composition ($1.09 < \text{Si/C} < 1.18$) and the TMS concentration ($0.07 < F_{\text{TMS}} < 0.21$) has no effect. This behavior could mean that these parameters act only on the fluxes of active species reaching the surface. According to the linear relationship between TMS flow and deposition rate, the growth process must be limited by the precursor decomposition.

In conclusion it is interesting to note that the surface aspect changes with composition : from bright and smooth for $\text{Si/C} > 1$, to dull and rough when $\text{Si/C} < 1$. Nevertheless all samples are dense as cross sectional fractures show no visible porosity.

3.- Properties and mechanical behavior

3.1.- Residual stresses.

In our case, the X-ray diffraction diagrams do not allow the evaluation of residual stresses, so they were estimated from the deflection 4 of foils coated with layers of different thickness. The total residual stresses are compressive and constant in the investigated range of thickness ($2 - 8\text{ }\mu\text{m}$). It was seen that, for the same thermal stresses ($\sigma_{\text{th}} \approx -1500\text{ MPa}$ at $T = 793\text{ K}$), the intrinsic stresses increase when total pressure decreases ($3000 < \sigma < 2000\text{ MPa}$, $100 < P < 1300\text{ Pa}$) that is with an increasing ion bombardment 5. Such a behavior was also seen by Classen et al in the case of silicon nitride films from a glow discharge process 6.

This results in a variation of the stored elastic energy which initiates spontaneous spallings for different threshold thickness (h_f) depending on the deposition conditions ($h_f = 8.5 \pm 0.5\text{ }\mu\text{m}$ when $P = 500\text{ Pa}$, $T = 873\text{ K}$; $h_f = 21.5 \pm 0.5\text{ }\mu\text{m}$ when $P = 1300\text{ Pa}$, $T = 873\text{ K}$).

3.2.- Hardness.

The vickers hardness values were determined on a shimadzu tester. They were calculated in a such a way to confine the plastic deformation zone inside the coating 7 and were corrected for the indentation size effect 8. The variation in function of the coating composition shows a maximum for $\text{Si/C} \approx 1$ 5. The sharp decrease observed for coatings with an excess of carbon unaccountable by a mixture law may be assumed to result of a peculiar microstructure (carbon localized at the grain boundaries), such a phenomenon has been recently observed with titanium carbide deposits 9.

3.3.- Scratch testing.

This test was applied on the samples to get a qualitative information on adherence between the coating and the substrate, using a classical progressive scratching device (CSEM) with acoustic emission. As a consequence of the numerous factors influencing the critical load values (L_c) related with film spalling there is no clear relationship with the work of adhesion; this is still a topic of debate 10-13. We tried to interpret our results through previous papers devoted to the understanding of this test 10-16.

In general the failure mode events are : plastic deformation, cracks formation and scaling or flaking 14. This sequence is observed when $\text{Si/C} > 1$. Internal transverse semicircular cracks begin to occur at low loads ($2\text{-}3\text{ N}$); their density increases with increasing loads. These cracks lead to cohesive failure (at this level iron is not detected inside the scratch tracks or at

the edges) due to Hertzian stresses around the stylus. According to the theory a maximum tensile stress must results at the rear of the contact ¹⁷. But taking into account the residual stresses in the coating (σ_r), the global resulting stress field can be reversed depending on the amount of σ_r and then compressive stress field may becomes prevailing. In a sliding sphere on plane contact the order of magnitude of stresses behind (σ_1) and ahead (σ_2) the indenter can be estimated from ^{17,18} :

$$\sigma_1 = \left[\frac{1-2\nu_2}{2} + \frac{3\pi}{16}(4+\nu_2)f \right] P_m \quad (1a)$$

$$\sigma_2 = - \left[\frac{1-2\nu_2}{2} + \frac{9\nu_2}{16}f \right] P_m \quad (2a)$$

$$\text{with } P_m = \frac{L}{\pi a^2} \text{ and } a^3 = \frac{3rL}{4} \left[\frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2} \right]$$

where E_1, ν_1, E_2, ν_2 are respectively the Young's modulus and Poisson's coefficient of the indenter ($E_1 = 1050$ GPa, $\nu_1 = 0,2$) and the coating, f ($f = 0,2$) is the friction coefficient with the considered surface, r the radius tip ($r = 200$ μm). As an example table 1 values come out.

	a (μm)	P_m (GPa)	σ_1 (MPa)	σ_2 (MPa)	σ_r (MPa)
Si-C	11.6	12.8	5650	-2300	-2400

Tab.1.- Si/C ≈ 1.17 with $E_2 = 380$ GPa from Scaff et al ¹⁹ and $\nu_2 \approx 0.2$.

A compressive stress state results ahead the sliding sphere, in accordance with the curvature of the cracks oriented in the direction of the increasing loads (from left to right) (figure 1).

Fig.1.- Film failure mode (Lc correspond to the white arrow).

For thick coatings a work of adhesion (W_{adh}) cannot be deduced from an energy balance approach ¹² because an unknown amount of energy is released by the cohesive cracks inside the scratch track. On the contrary, for thin layers ($h_f < 2$ μm) such a balance may be applied since scaling occurs at a low critical load when almost no cracking is visible in the track. In this way, results are presented in table 2.

	Si/C (at.)	E (GPa)	h_f (μm)	σ_r (MPa)	L_c (N)	σ_2 (MPa)	W (J.m ⁻²)
Si-C	1.14	390	1.7	-2850	2.2	-2100	53
Si-C	1.10	395	1.2	-3200	2.0	-2050	42

Tab.2.- Work of adhesion calculated by an energy balance.

The values so-obtained are close to those encountered for TiC and/or TiN¹⁰, though the low measured critical loads.

Systematic measurements of critical loads ($L_c \pm 5\%$) on samples reveal a maximum in function of the composition (table 3).

	Si/C (at)	E (GPa)	Hv (GPa)	H_v^2/E (GPa)	T (K)	P (Pa)	σ_r (MPa)	L_c (N)
1	1.34	340	23	1.56	673	500	-1950	7.3
2	1.25	360	29	2.32	773	500	-2300	8.4
3	1.18	370	30	2.43	873	1300	-2400	8.9
4	1.14	390	32	2.62	873	500	-2800	7.9
5	1.02	430	36	3.02	973	500	-3350	7.2

Tab.3.- Variation of measured critical load (sample of identical thickness $h_f \approx 7.5 \mu\text{m}$).

Respectively it was observed that the increase in L_c between samples 1 and 3 was associated with more cohesive cracks inside the track. As other properties also vary the relation with adherence is not direct, and the question has been to know if there is really an increasing adherence when the excess silicon content decreases and how to explain it. The energy balance based on the fact that the coating loss occurs when the stored energy (considered as the sum of three terms : frictional, indentation and internal) is higher than the surface energy required to form the crack¹² does not fit with the observed trend. Assuming a constant frictional contribution, from the values reported in table 3, when the silicon content decreases the indentation and internal energy terms increase and thus a decrease in L_c would result. In this case the opposite experimental variation could signify an increasing adherence. But now if it is postulated that the released energy is used to provide the surface energy for the adhesive and cohesive crack formation (the area in non spallation cracking is macroscopically larger than in the spallation events) as the density of fracture events increases (from sample 1 to 3), energy is more consumed in this failure mode and then an increasing L_c would be required to produce coating detachment.

4.- Approach of the interface.

At this stage of the study where the measurements tend to denote a good adherence, one of the questions we tried to answer is whether a chemical driving force is noticeable.

With such a purpose Auger sputter profiling was carried out on very thin samples prepared specifically for this analysis (AES).

On the basis of the experimental linear relationship between time and deposition rate, coatings of about 0.2 micron thick were prepared in short runs (15 s) and then annealed in

argon plasma flow for 15 mn. This procedure could lead to an interfacial situation similar to the one encountered in thick coatings (sample 3) obtained by a 15 mn experiment.

Auger measurements were performed in a SIA-200 RIBER U-H-V device. A MICROFOKUS EK-15-M electron gun excited the Auger transitions.

Auger electrons were analyzed by a RIBER MAC-2 two stage analyzer system having a constant resolution. Depth profile was carried out by Argon ion sputtering, with an accelerating voltage of 3 kV, and an ion current density of about $15 \mu\text{A.cm}^{-2}$.

Two kinds of spectra were scanned. First acquired in the energy range 0-750 eV; in this case, the electron primary energy was fixed at $E_p = 3 \text{ keV}$ and the analyzer resolution at 1 eV. The second AES spectra were scanned in the high kinetic energy range 1600-1650 eV to detect the core-core transition Si $\text{KL}_{23}\text{L}_{23}$. Operation conditions were : primary energy $E_p = 5 \text{ keV}$ and analyzer resolution 2 eV.

In order to get a good relative information from the $E.N(E)$ distribution, we determined the Auger ratio P/B (ratio to the height of the Auger peak to the background at the same energy) which depends only on the primary electron energy. Furthermore it is worthwhile to mention that the acquisition were made under argon bombardment. The first result we got after 10 mn of sputter etching (3 keV Ar^+) of a sample ($\text{Si/C} \approx 1.2$) is presented in figure 2.

Fig.2.- AES spectrum [$dE.N(E)/dE$] of the thin CVD sample.

From the derivate AES spectrum it is clear that the sample does not exhibit a significant contamination by oxygen. The carbon peak KVV is typical of a carbide as compared to a standard monocrystal. Though the sputter time is low, the main Fe Auger peaks begin to appear. This will be discussed afterwards. The in-depth information is summarized by figure 3 for the different elements involved in the system.

Fig.3.- Sputtering depth profile of the thin CVD layer on 35CD4 steel.

The overall shape of the profile leads to the distinguishing of two parts : (I) a short plateau followed by a region (II) in which Si and C are decreasing meanwhile Fe increases.

It is worthwhile to mention that the P/B ratio obtained for the last measurement (sputter time 190 mn) is very close to the value determined for the pure bulk substrate (0,27). At this level such a profile may suggest a phenomenon of diffusion. In order to be sure, the position of the Si $KL_{23}L_{23}$ transition was examined.

The results (figure 4a) evidence a significant 1.5 ev shift of the N(E) Si $KL_{23}L_{23}$ peaks towards an increasing energy as sputtering proceeds. Such a shift is also visible on the valence band Si $L_{23}VV$ which lies at 92 ev for pure silicon. The shift would be in good agreement with the change from Si-C bonds (zone I in figure 3) to Si-Si or Si-Fe bonds (zone II in figure 3). This shift can be attributed to an increase in electron density near the Fermi level of Si when the Si atoms are bonded to less electron negative elements. We observed an identical shift between a standard sample of SiC and pure silicon.

On the other hand, the evolution of the C KVV line, though weakest, is nevertheless visible when comparing different spectra in regards to standard samples presented in figure 4b where are shown a reference [monocrystalline α - SiC (4)] a thick SiC deposit obtained in the same conditions that the sample sputtered in this work (5) and some spectra recorded for different sputter times (amplitudes are not normalized).

Fig.4a.- Variation of Si KLL Auger spectra.

Fig.4b.- Variation of C KVV Auger spectra.

The C KVV transition shape after 10 mn of sputtering (1) is very similar to that of SiC standards (4) and (5). These features disappear for the points relative to zone II in figure 3 illustrated by the C KVV spectra 2 and 3 in figure 4.

All the aforementioned changes are in favour of an intermediate layer formed in between substrate and deposit. Previous experimental studies on diffusion couple 20 at 1123 K reveal a sequence $SiC / \alpha(Fe,Si)+C / \alpha(Fe,Si) / Fe$ associated with a quite normal diffusion path in the ternary phase diagram. So zone II must essentially correspond to a biphased field since carbon is clearly detected. Due to the lack of precision the pure $\alpha(Fe,Si)$ is unidentified. Its presence could be ranged for sputter times beyond 160 mn. The very low content of Fe at the beginning of the in-depth measurements could be related to the fact that only iron migrates; it could reach the surface vicinity through porosities in the thin layer or grain boundaries.

The same kind of analysis was performed on the cross section of a diffusion couple (SiC/Fe prepared at 1123 K). The line scan realized by moving the sample step by step of about 10 μm is reported in figure 5.

Fig.5.- Line scan of a cross section of SiC/Fe diffusion couple after sputter cleaning (primary electron energy 5 keV).

The oxygen signal can be recognized on all the spectra, this means an higher bulk amount of contamination than in the CVD experiments. The surface contamination layer was removed by bombardment with argon ions of 3 keV primary energy during 15 mn resulting in a sputter cleaned surface. The variation in content of the elements through the thickness is clear. Through the highest P/B values consecutive to a higher primary beam energy (5 keV), the trend corroborates the in-depth sputtered results.

5.- Friction and wear behavior.

Wear and friction tests were performed using a reciprocating pin on flat device at constant sliding speed (26.4 mm.s⁻¹) in ambient air. The hemispherical-shaped pin (35NCD16, 1800 MPa, radius of curvature 10 mm) was moved along 4.4 mm under a normal load of 3 N. Figure 6 shows the typical variation of the friction coefficient for the different tested samples. After a transition period which is associated with metallic transfers and the formation of wear fragments a steady state regime occurs with a constant friction coefficient (0.4).

Fig.6.- Variation of the friction coefficient (Si/C $\approx$ 1.2)

By measuring the wear scar of the pin as a function of the sliding distance (or cycles) two behaviors were observed : firstly a strong abrasive wear followed after several thousand cycles by a light wear. SEM observations of the wear scars of steel pins reveal surfaces covered by scratches and adherent products of different contrast which denote a transfer layer from disc to pin. Such a phenomenon was previously observed in the pair 35CD4-PVD WC²¹.

By auger analysis silicon oxide and iron oxide were detected. This latter only in the central area. On the coated surface the wear scar is smooth just with small scratches due probably to transferred particles. During this test, as a consequence of the pin wear, the spherical/plane contact becomes a plane/plane contact with a different stress field distribution and then local enhanced stresses along the contact edges could explain the wear profile.

6.- Conclusion.

Plasma assisted CVD from $\text{Si}(\text{CH}_3)_4$ -Ar mixtures allows the deposition of hard coatings whose properties can be varied as a function of the Si/C ratio in the deposits. A controlled excess of silicon can be easily obtained through the variation of the deposition temperature or pressure and leads to a qualitatively good adherence in contrast with the samples presenting a carbon excess, even when very slight. This behaviour is correlated with a chemically different interfacial zone as it was detected by in-depth Auger analysis.

Acknowledgments

The authors wish to thank Pr. F. Van Loo (Technical University of Eindhoven) for providing the diffusion couple (Fe/SiC), Dr. P. Kapsa (Ecole Centrale de Lyon) for welcoming us to carry out the tribological tests.

This work was supported jointly by CNRS and DRET.

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